Indian Journal of Chemistry
Vol. 15A, July 1977, pp. 605-607

Kinetics & Mechanism of Oxidation of Aromatic Amines by Peroxydisulphate: Part V—Role of Substituents on Reactivity

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Received 8 *October* 1976; *accepted* 7 *January* 1977

The kinetics of the reaction between different mono- and di-substituted anilines and peroxydisulphate ion in acetic acid medium have been investigated and various thermodynamic parameters are calculated. The reaction is accelerated by electron-withdrawing substituents and retarded by mono- and di-methyl substituents. A better correlation, between rate and the Hammett constant, is obtained for a rate-limiting attack at the nitrogen atom of the amino group rather than at the carbon atom carrying the amino group of the amine. Hammett constant (ρ) is found to be +1·88. The validity of isokinetic relationship has been tested.

THE kinetics of reaction between aromatic amines and peroxydisulphate in aqueous base (Boyland-Sims oxidation[1-4]) was investigated by Behrman[5]. Later Venkatasubramanian and Sabesan[6] studied substitutent effects on the reaction rate and proposed a mechanism involving a nucleophilic displacement by the amine nitrogen on the peroxide oxygen to yield the corresponding *o*-aminoaryl sulphates. However, it was found by us that the coloured product formed in the early stages of the reaction remained dissolved in acetic acid medium[7] and that N-phenyl-*p*-benzoquinonediimine (N-PBD) and N-tolyl-*p*-toluquinonediimine (N-TTD) are the initial products in the oxidation of aniline[8] and *o*-toluidine[9] respectively. The N-PBD remains dissolved in acetic acid medium for a considerable length of time in the early stages of the reaction and then polymerizes in the presence of $S_2O_8^{2-}$ to give a polymeric substance (major product), and also side by side undergoes hydrolytic decomposition to give *p*-benzoquinone; the latter then condenses with aniline to give 2,5-dianilino-*p*-benzoquinone and other side products in traces (detected by TLC[8-10]). It may be mentioned that free radicals are involved in the reaction, as found[8,9] by the appreciable inhibitory action of allyl acetate and allyl alcohol. In order to have a better insight of the reaction mechanism, and the substituent effects, the study has been extended to other mono- and disubstituted anilines.

Materials and Methods

Potassium peroxydisulphate and acetic acid of GR (E. Merck) were used after recrystallization and redistillation respectively. The various anilines (AR) were used after recrystallization or redistillation. The reaction was studied spectrophotometrically in acetic acid (0·8*M*) as described earlier[7].

Results and Discussion

The rate constants were evaluated by Sturtevent's method as explained earlier[8]. The second-order rate constants for the oxidation of a number of mono- and disubstituted anilines are presented in Table 1. It is evident that electron-withdrawing substituents on aniline accelerate the reaction whereas the rate is appreciably retarded by electron-donating substituents like the methyl group.

The correlation of these data with the Hammett substituent constants[11,12] is shown in Figs. 1 and 2. The data are plotted in two ways. Fig. 1 assumes rate-limiting attack at nitrogen while Fig. 2 assumes rate-limiting attack at carbon. One might expect that for the *meta*-substituted anilines, rate-limiting attack at nitrogen should correlate with σ_m while rate-limiting attack at the carbon *para*- to the *meta*-substituent would give a good correlation of log k_2 with σ_p of the substituents. It is known that the carbon atom between NH_2-group and *meta*-substituent is not attacked, as steric consideration weigh against this[2]. Similarly for *p*-substituted anilines, attack at the nitrogen would be expected to correlate better with σ_p while attack at the carbon carrying the amino function should give a correlation with the *meta*-substituent constants. Further, for the *ortho*-substituted anilines, the attack on nitrogen should show a correlation between the logarithm of the rate constants and σ_o while for attack on carbon the same rate constants should be correlated with σ_m for the same substituents. The substituent constant values for *meta*- and *para*-substituents were taken from the work of McDaniel and Brown[13] and for *ortho*-substituents these were calculated by the least squares method using Clark and Perrin's equation[14].

The data in Figs. 1 and 2 show that a good overall correlation exists only for the plot that assumes attack at the nitrogen rather than at carbon *ortho* to the nitrogen. Further the correlation coefficient, standard deviation and the error in reaction constant, calculated on this basis using standard equations[15], come out to be 0·9692, 0·17 and 0·14 respectively, which point to a fairly good correlation. In fact, the points for the second plot for an assumed attack on carbon show random scatter and one cannot discern any linear relationship here. The Hammett's

TABLE 1 — KINETIC AND THERMODYNAMIC PARAMETER FOR THE OXIDATION OF VARIOUS ANILINES

{[Amine]=0·01M; ($S_2O_8^{2-}$]=0·0025M; [Acetic acid]=0·08M; temp.=40°}

Aniline	λ_{max} (nm)	σ	$k_2\times10^2$ (litre mole^{-1} sec^{-1})	$A\times10^{-9}$ (litre mole^{-1} sec^{-1})	$\Delta E^{\ddagger}$ (kcal mole^{-1})	$-\Delta S^{\ddagger}$ (e.u.)	$\Delta H^{\ddagger}$ (kcal mole^{-1})	$\Delta F^{\ddagger}$ (kcal mole^{-1})
H	405	0·00	1·45	7·29	15·83	15·86	15·54	20·50
o-Me	530	−0·136	0·82	9·93	16·34	15·27	15·73	20·51
m-Me	515	−0·069	0·53					
p-Me	500	−0·170	0·61					
o-Et	530	−0·199	0·63					
o-OMe	420	−0·574	16·11	0·30	13·27	17·63	13·98	19·50
o-COOH	435	0·254	4·21	10·5	16·40	15·18	15·76	20·51
m-COOH	395	0·370	10·79	0·88	14·16	20·08	13·49	19·77
p-COOH	410	0·450	5·02	3·14	15·46	17·57	14·91	20·41
o-OH	410	0·869	55·56					
p-Cl	410	0·227	8·19	11·09	15·91	15·04	15·25	19·96
m-Br	420	0·391	4·37	0·87	14·75	20·09	14·08	20·37
3,4-Me_2	405	−0·239	0·56					
2,4-Me_2	510		1·00					
p-OMe	550		24·21*					

*Value obtained at 10°C.

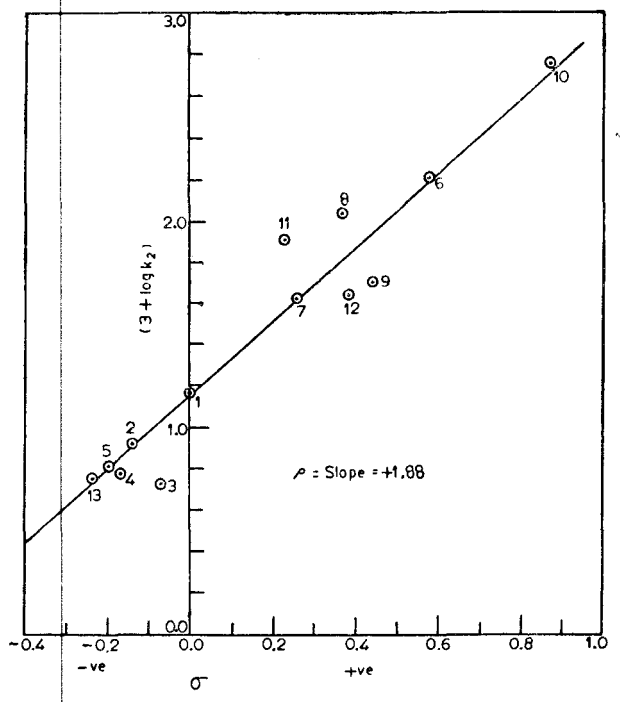


Fig. 1 — Correlation of Hammett substituent constants with second order rate constants assuming rate limiting attack at nitrogen [(1) H; (2) *o*-CH_3; (3) *m*-CH_3; (4) *p*-CH_3; (5) *o*-C_2H_5; (6) *o*-OCH_3; (7) *o*-COOH; (8) *m*-COOH; (9) *p*-COOH; (10) *o*-OH; (11) *p*-Cl; (12) *m*-Br; and (13) 3,4-Me_2]

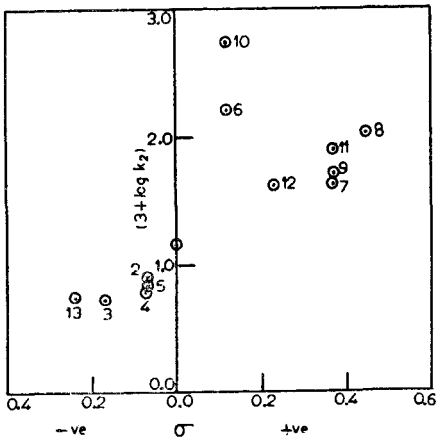


Fig. 2 — Correlation of Hammett substituent constants with second order rate constants assuming rate limiting attack at carbon carrying amino function [Arabic numerals refer to substituents listed in Fig. 1]

ρ for the oxidation of substituted anilines in acetic acid medium comes out to be +1·88 while the values of ρ for the peroxydisulphate oxidation of aromatic amines in alkaline medium has been reported as −1·30 by Behrman[5] and −1·41 by Venkatasubramanian and Sabesan[6].

A positive value of ρ for the present systems indicates that the reaction is favoured by the presence of electron-withdrawing groups in the benzene ring. The thermodynamic parameters for different substituted anilines are recorded in Table 1.

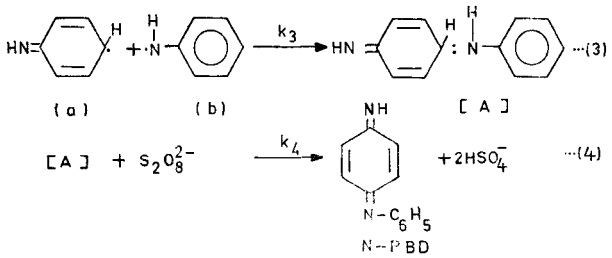
The values of $\Delta H^{\ddagger}$ were plotted against the corresponding $\Delta S^{\ddagger}$ values in order to test the validity of isokinetic relationship. It is found that the points corresponding to various substituents lie on a linear plot (isokinetic line), the correlation coefficient being 0·99. Only three points corresponding to *o*-OMe, *m*-COOH and *p*-Cl, deviate from the isokinetic line, which may be attributed to experimental errors. The slope β of the isokinetic line, as calculated by method of least squares, is 343°K which is the isokinetic temperature for the present reaction series. Since this value of β (343°K) considerably differs from the experimental temperature (303°K), the linearity between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values cannot be attributed to the experimental errors involved in the determination of these values[16,17]. Hence, it is reasonable to conclude that various substituted anilines studied presently undergo oxidation by a similar mechanism.

Thus, on the basis of the kinetic results[8,9] and the fact that the present series of reaction obeys

Hammett's equation and isokinetic relationship fairly well and the various thermodynamic parameters have almost similar values for different substituted anilines, we propose the following general mechanism (Eqs. 1-4) for the oxidation of aromatic amines by $S_2O_8^{2-}$ in acetic acid medium, taking aniline as a typical example:

$$S_2O_8^{2-} + C_6H_5NH_2 \xrightarrow{k_1} C_6H_5\dot{N}H + S\dot{O}_4^- + HSO_4^- \quad ...(1)$$

$$S\dot{O}_4^- + C_6H_5NH_2 \xrightarrow{k_2} C_6H_5\dot{N}H + HSO_4^- \quad ...(2)$$



...(3)

...(4)

The $C_6H_4\dot{N}H$ radical resonates in the forms (a) and (b), which then react according to Eq. (3).

Applying steady state treatment to the radicals, $C_6H_5\dot{N}H$, SO_4^- and A, we have the kinetic expression (5) for the rate of formation of N-PBD.

$$d/dt[P] = 2k_1[C_6H_5NH_2][S_2O_8^{2-}] \quad ...(5)$$

The above expression is in accordance with the kinetic results obtained.

Thus, in conclusion, it may be stated that on the basis of various kinetic features and study of various intermediates[8] and end products[10], it can reasonably be assumed that the oxidation of aromatic amines by $S_2O_8^{2-}$ in acetic acid medium, first leads to the formation of N-phenyl-*p*-benzoquinonediimine (or of a compound corresponding to the amine taken), which then polymerizes in presence of $S_2O_8^{2-}$ to give the polymeric substance as the major product and also side by side undergoes hydrolytic decomposition to give *p*-quinone, the latter then condenses with the corresponding amine to form various condensation products. The nature of the polymeric substance, which may be the result of one or more series of condensation processes, is under study.

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